

PCT

WELTORGANISATION FÜR GEISTIGES EIGENTUM
Internationales Büro



INTERNATIONALE ANMELDUNG VERÖFFENTLICH NACH DEM VERTRAG ÜBER DIE
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

<p>(51) Internationale Patentklassifikation⁶ : C08F 26/06, A61K 7/06</p>		<p>A1</p>	<p>(11) Internationale Veröffentlichungsnummer: WO 95/15986</p> <p>(43) Internationales Veröffentlichungsdatum: 15. Juni 1995 (15.06.95)</p>
<p>(21) Internationales Aktenzeichen: PCT/EP94/04027</p> <p>(22) Internationales Anmeldedatum: 3. December 1994 (03.12.94)</p> <p>(30) Prioritätsdaten: P 43 42 281.0 11. December 1993 (11.12.93) DE</p> <p>(71) Anmelder (<i>für alle Bestimmungsstaaten ausser US</i>): BASF AKTIENGESELLSCHAFT (DE/DE); D-67056 Ludwigshafen (DE).</p> <p>(72) Erfinder; und (75) Erfinder/Anmelder (<i>nur für US</i>): BLANKENBURG, Rainer [DE/DE]; Irisstrasse 10, D-67067 Ludwigshafen (DE). SANNER, Axel [DE/DE]; Lorscher Ring 2c, D-67227 Frankenthal (DE).</p> <p>(74) Gemeinsamer Vertreter: BASF AKTIENGESELLSCHAFT; D-67056 Ludwigshafen (DE).</p>		<p>(81) Bestimmungsstaaten: CA, JP, US, europäisches Patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Veröffentlicht <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist. Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i></p> <p>2178328</p>	
<p>(54) Title: PROCESS FOR PRODUCING POWDERY POLYMERS BASED ON N-VINYL CAPROLACTAMS</p> <p>(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON PULVERFÖRMIGEN POLYMERISATEN AUF DER BASIS VON N-VINYLCAPROLACTAM</p> <p>(57) Abstract</p> <p>Powdery polymers based on n-vinyl caprolactams are produced by polymerising (A) 50 to 100 % by weight N-vinyl caprolactams with (B) 0 to 50 % by weight other N-vinyl lactams, vinyl heteroaromatics, vinyl esters, C₁ to C₁₀ alkyl acrylates or methacrylates or a mixture thereof and (C) 0 to 5 % by weight monoethylenically unsaturated monomers containing acid groups. For that purpose, (i) the monomers A, B and C are polymerised in a homogenous aqueous solution that contains 10 to 95 % by weight, in relation to the water, of a water-miscible organic solvent, or in a homogeneous mixture of 0 to 90 % by weight water and 100 to 10 % by weight methanol in the presence of a radical-forming initiator, and water is then substituted for the organic solvent; or (ii) the monomers A, B and C are polymerised in an aqueous emulsion in the presence of a radical-forming initiator and if required in the presence of an emulsifier. The thus obtained aqueous polymer solutions or dispersions are subjected to a usual drying process to produce powdery polymers.</p> <p>(57) Zusammenfassung</p> <p>Herstellung von pulverförmigen Polymerisaten auf der Basis von N-Vinylcaprolactam durch Polymerisation von (A) 50 bis 100 Gew.-% N-Vinylcaprolactam mit (B) 0 bis 50 Gew.-% weiterer N-Vinylactame, Vinylheteroaromat, Vinylester, C₁- bis C₁₀-Alkylacrylate oder -methacrylate oder einer Mischung hieraus und (C) 0 bis 5 Gew.-% Säuregruppen enthaltender monoethylenisch ungesättigter Monomere, indem man die Monomere A, B und C (i) in homogener wasserhaltiger Lösung, die 10 bis 95 Gew.-%, bezogen auf das Wasser, eines wasserlöslichen organischen Lösungsmittels enthält, oder in einem homogenen Gemisch aus 0 bis 90 Gew.-% Wasser und 100 bis 10 Gew.-% Methanol in Gegenwart eines radikalbildenden Initiators polymerisiert und anschließend das organische Lösungsmittel gegen Wasser austauscht oder (ii) in wässriger Emulsion in Gegenwart eines radikalbildenden Initiators und gegebenenfalls in Gegenwart eines Emulgators polymerisiert und die so erhaltenen wässrigen Polymerisationslösungen oder -dispersionen einem hierfür üblichen Trocknungsverfahren zur Erzeugung pulverförmiger Polymerisate unterwirft.</p>			

BEST AVAILABLE COPY

Preparation of pulverulent polymers based on N-vinylcaprolactam

The present invention relates to an improved process for the
5 preparation of pulverulent polymers based on N-vinylcaprolactam
by polymerizing

- A) from 50 to 100% by weight of N-vinylcaprolactam with
- 10 B) from 0 to 50% by weight of further N-vinylactams, heteroaromatic vinyl compounds, vinyl esters, C₁-C₁₀-alkyl acrylates or methacrylates, or a mixture thereof, and
- 15 C) from 0 to 5% by weight of monoethylenically unsaturated monomers containing acid groups.

In the field of hair cosmetology there is particularly strong interest in solid, ie. pulverulent, polymers which are free from organic solvents, such as alcohols, since as a result of the ever 20 tightening worldwide statutory regulations regarding organic solvents and propellants in hairsprays and similar products the demand is almost exclusively now for only those polymers which have been prepared on a purely aqueous basis. Furthermore, solid polymers generally have handling advantages over solutions or 25 dispersions; problems which may be mentioned in this context are, in particular, the problem of contamination, especially of aqueous polymer solutions, with microorganisms during storage, and the problem of transportation, owing to the greater weight.

30 In the field of hair cosmetology, polyvinylcaprolactam and copolymers thereof with usually relatively small quantities of comonomers are known to be film formers having outstanding properties. However, such polymers are also used in other technical fields.

35

The Journal of Applied Polymer Science, Vol. 12 (1968), pp. 1835-1842 (1) discloses that above about 30 to 35°C polyvinylcaprolactam which has been prepared by bulk polymerization or solution polymerization in toluene is 40 precipitated from its aqueous solutions. US-A 4 521 404 (2) reveals that copolymers of N-vinylcaprolactam, for example with N-vinylpyrrolidone, prepared by solution polymerization in anhydrous ethanol followed by distillation to remove the solvent, behave similarly and give rise at least to instances of 45 cloudiness when the corresponding aqueous solutions are heated gently, for example to about 55°C in the case of a 1:1 by weight N-vinylcaprolactam-N-vinylpyrrolidone copolymer. In general, such

precipitates are obtained as rubberlike solids which can no longer be handled. This prejudice concerning the impossibility of preparing a pulverulent, easily handled N-vinylcaprolactam polymer by this method has so far prevented the drying of such 5 polymers from aqueous solution by means of industrial drying techniques which are customary for such polymers, since these techniques generally entail the heating - at least for a short time - of these aqueous solutions.

10 WO 92/17509 (3) shows us the possibility of preparing solid pulverulent N-vinylcaprolactam polymers, for example N-vinylcaprolactam homopolymer or N-vinylcaprolactam-acrylic acid copolymer by precipitation polymerization from organic solvents such as alkanes and cycloalkanes, examples being heptane or 15 cyclohexane.

It is an object of the present invention to provide a process for preparing pulverulent N-vinylcaprolactams from a solution which is aqueous or can be converted to an aqueous solution, for which 20 it is possible to employ customary industrial drying techniques.

We have found that this object is achieved by the process defined at the outset, which comprises subjecting the monomers A, B and C

25 (i) to polymerization in homogeneous, water-containing solution, which contains from 10 to 95% by weight of a water-miscible organic solvent, based on the water, or in a homogeneous mixture comprising from 0 to 90% by weight of water and from 100 to 10% by weight of methanol, in the presence of a 30 free-radical initiator, and then replacing the organic solvent by water, or

(ii) to polymerization in aqueous emulsion in the presence of a free-radical initiator and in the presence or absence of an 35 emulsifier

and subjecting the resulting aqueous polymer solutions or dispersions to a drying technique which is customary for such formulations, in order to produce pulverulent polymers.

40 In a preferred embodiment, polymerization in (ii) is carried out in the absence of a monomer C but in the presence of an emulsifier. However, if at least 30% by weight, based on the overall quantity of the monomers, of a further N-vinylactam is 45 present as monomer B, the use of an emulsifier in the polymerization is preferably omitted.

Suitable monomers B are further N-vinyl lactams, especially N-vinylpyrrolidone and N-vinylpiperidones, heteroaromatic vinyl compounds, especially N-vinylimidazole and vinylpyridines or vinylpyridine N-oxides, vinyl esters, especially vinyl acetate 5 and vinyl propionate, and also C₁-C₁₀-alkyl (meth)acrylates, especially methyl, ethyl or butyl acrylate or the corresponding methacrylate.

Suitable monomers C are monoethylenically unsaturated compounds 10 containing at least one acid group, for example a carboxyl group, a sulfonic acid group or a phosphonic acid group. Examples of such compounds are acrylic acid, methacrylic acid, dimethacrylic acid, ethylacrylic acid, crotonic acid, allylacetic acid or vinylacetic acid. Other suitable compounds are monoethylenically 15 unsaturated dicarboxylic acids, for example maleic acid, fumaric acid, itaconic acid, mesaconic acid, methylenemalonic acid, citraconic acid, maleic anhydride, itaconic anhydride and methylenemalonic anhydride, the anhydrides normally hydrolyzing to form the corresponding dicarboxylic acids on introduction into 20 water. Also suitable as monomers C are monomers containing sulfonic acid groups, examples being 2-acrylamido-2-methylpropanesulfonic acid, 3-sulfopropyl (meth)acrylate, vinylsulfonic acid, methallylsulfonic acid or allylsulfonic acid, and monomers containing phosphonic acid 25 groups, such as vinylphosphonic acid. The monomers C can be employed either alone or in a mixture with one another.

Preferred monomers C are acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, 30 2-acrylamido-2-methylpropanesulfonic acid, vinylsulfonic acid, 3-sulfopropyl acrylate or methacrylate, and vinylphosphonic acid.

In the polymerization the monomers C can be employed either in the form of the free acids or, preferably, in the form of their 35 alkali metal, alkaline earth metal or ammonium salts. It is advantageous to employ these salts of the monomers C as aqueous solutions. In this context, particularly important cations are sodium, potassium, magnesium and calcium, but also lithium, strontium and barium. The salts of the monomers C are normally 40 prepared by customary neutralization of the acids in an aqueous medium.

In a preferred embodiment, the polymers employed comprise

- A) from 90 to 100% by weight, in particular from 95 to 100% by weight, of N-vinylcaprolactam with
- 5 B) from 0 to 10% by weight, in particular from 0.1 to 5% by weight, of the monomers B and
- C) from 0 to 5% by weight, in particular from 0.1 to 3% by weight, of the monomers C.

Particular preference is given to copolymers comprising

- A) from 95 to 99.9% by weight, in particular from 97 to 99.5% by weight, of N-vinylcaprolactam with
- 15 C) from 0.1 to 5% by weight, in particular from 0.5 to 3% by weight, of the monomers C,

20 it being possible to prepare these copolymers in accordance with embodiment (i) or in accordance with embodiment (ii), preferably without emulsifier.

Particular preference is also given to homopolymers comprising 25 100% by weight of N-vinylcaprolactam A, it being possible to prepare these polymers preferably in accordance with embodiment (i) in pure methanol, or preferably in accordance with embodiment (ii) with emulsifier.

30 Where polymerization is carried out in accordance with embodiment (i) in a homogeneous mixture of water and a water-miscible organic solvent, use is preferably made of a C₂-C₄-alkanol, especially ethanol or isopropanol. In this case the proportion of organic solvent, based on the water, is from 10 to 95% by weight, 35 preferably from 25 to 85% by weight and, in particular, from 50 to 75% by weight.

The use of water/methanol mixtures, and especially of pure methanol, in embodiment (i) is particularly advantageous for the 40 preparation of N-vinylcaprolactam homopolymers or of copolymers of N-vinylcaprolactam with further N-vinylactams B, especially with N-vinylpyrrolidone.

In both embodiments (i) and (ii) the concentration of the 45 polymers in the aqueous reaction mixture is usually from 10 to 70% by weight, preferably from 15 to 50% by weight. The pH of the aqueous solution is at least 6 and is preferably in the range

from 7 to 9, the pH of the aqueous reaction solution generally being established by the addition of an alkali metal base or alkaline earth metal base. In this context the simplest procedure is to employ the monomers C as aqueous solutions of their alkali 5 metal, alkaline earth metal or ammonium salts with a pH of at least 6. However, it is also possible to add the monomers C in unneutralized form to the reaction mixture and to add at the same time an at least equivalent quantity of a corresponding base in order to bring the pH of the reaction mixture into the desired 10 range of 6 or more.

Polymerization is generally carried out at from 40 to 150°C, preferably at from 60 to 100°C, under atmospheric pressure or superatmospheric pressure, in the presence of free-radical 15 initiators. These polymerization initiators are normally added in quantities of from 0.01 to 20% by weight, preferably from 0.05 to 10% by weight, based on the monomers.

Suitable free-radical initiators are commonly all those compounds 20 which have a half life of less than 3 hours at the particular polymerization temperature which is chosen. Preference is given to water-soluble and ionic initiators, examples being hydrogen peroxide, sodium persulfate, potassium persulfate, ammonium persulfate, 2,2'-azobis(N,N'-dimethyleneisobutyramidine) 25 dihydrochloride, 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(dimethyl isobutyrate), 4,4'-azobis(4-cyanopentanoic acid) and tert-butyl perpivalate.

Compounds which are less preferred, but which can also be 30 employed in certain circumstances, are those polymerization initiators which are insoluble or of only limited solubility in water, such as tert-amyl perpivalate, dioctanoyl peroxide, dilauroyl peroxide, 2,2'-azobis(2,4-dimethylvaleronitrile), dibenzoyl peroxide, tert-butyl per-2-ethylhexanoate, tert-amyl 35 per-2-ethylhexanoate, tert-butyl permaleate or 2,2'-azobis(isobutyronitrile), and also redox initiators, such as heavy metal salt-hydrogen peroxide systems.

In general, a suitable base is used to neutralize the aqueous 40 solution of the polymerization initiators before it is added to the polymerization medium.

The molecular weight of the polymers can be controlled by adding regulators to the reaction mixture, control in most cases 45 implying reduction. Therefore, in a preferred embodiment of the invention in (ii), a regulator is additionally employed in order to control the molecular weight. Examples of suitable regulators

are lower alcohols such as methanol, ethanol, propanol, n-butanol, isopropanol, isobutanol and pentanol. However, other suitable molecular weight regulators are those compounds which are customarily employed for this purpose, such as organic sulfur compounds, for example 2-mercaptoethanol, butyl mercaptan, dodecyl mercaptan, thioacetic acid or thiolactic acid, halogen compounds, for example carbon tetrachloride or 1,1,1-tribromopropane, or formic acid and derivatives thereof.

10 An appropriate choice of regulator, initiator, polymerization temperature and monomer concentration establishes the K value of the polymer obtained, which is a measure of the molecular weight. The Fikentscher K values of the resulting polymers are usually from 10 to 300, preferably from 15 to 200, and are measured on a 15 1% strength by weight aqueous solution at 25°C (in accordance with H. Fikentscher, *Cellulose-Chemie*, Volume 13 (1932), pp. 58-64 and 71-74).

Suitable emulsifiers which may be required for embodiment (ii) 20 are all systems which are customary for this type of polymerization with virtually no restriction. Suitable emulsifiers in this context include neutral, anionic and cationic types. A wide variety of such emulsifiers is described in the literature, for example in the article by R. Hensch in Ullmann's 25 *Encyclopedia of Industrial Chemistry*, 5th edition (1987), Volume A9, pp. 297-339.

Examples of emulsifiers which can be employed successfully are anionic compounds, especially alkali metal, ammonium and amine 30 salts of relatively long-chain fatty acids, alkali metal salts of sulfuric esters of fatty alcohols and fatty alcohol ethers, for example sodium lauryl ether sulfate, with from 1 to 15 mol of ethylene oxide, and of alkylphenols, alkali metal salts of dialkyl sulfosuccinates, and also alkali metal salts of the 35 sulfonic acids of alkylbenzenes, for example sodium dodecyl sulfate, alkylnaphthalenes and of naphthalene. However, it is also possible to use cationic compounds, examples being fatty amines, quaternary ammonium compounds or quaternized pyridines, morpholines or imidazolines. Other highly suitable compounds are 40 polyol fatty acid esters reacted with from 2 to 30 mol of ethylene oxide, for example sorbitan monooleate with 20 mol of ethylene oxide. It is common to employ mixtures of different types of emulsifier.

45 In the presence of monomers C it is not necessary in principle to add an emulsifier, since the ionic groups in the monomers C themselves have emulsifier properties in respect of the monomers

and/or of the polymers formed therefrom. However, in such a case the addition of a customary emulsifier may not be disadvantageous, and in some cases even facilitates the polymerization process.

5

The polymerization reaction is generally carried out in stirred reactors fitted with anchor, paddle, impeller or multistep pulsed countercurrent stirrers. Where high concentrations are employed, it is advantageous to use compounders or similar apparatus. For 10 polymerization it is possible to charge the entire batch to the reactor and, after heating it to the desired temperature, to start the reaction by adding the initiator. With this procedure, however, the dissipation of the heat of polymerization presents problems. It is more advantageous, therefore, to charge the 15 solvent to the reactor and to meter in the monomers, in undiluted form or as an aqueous monomer solution, and the initiator, as a solution in water or alcohol, in portions or continuously, at the chosen polymerization temperature. It is often also of advantage for the progress of the reaction to charge the solvent to the 20 reactor and to meter in the monomers, the initiator and the neutralizing agent required to maintain the necessary pH under the polymerization conditions.

The replacement of organic solvent by water in embodiment (i) is 25 normally carried out by adding the appropriate quantity of water to the reaction batch after polymerization has been carried out and after simultaneous or subsequent removal of the solvent by distillation under atmospheric or subatmospheric pressure. It is particularly advantageous to separate off the organic solvent by 30 steam distillation.

Suitable drying techniques for the production of pulverulent polymers are all those techniques which are suitable for drying aqueous solutions. Preferred techniques are spray drying, 35 fluidized-bed spray drying, roller drying and belt drying, while less preferred but equally possible techniques are freeze drying and freeze concentrating.

The polymer powders obtainable in accordance with the invention 40 by drying from aqueous solution are soluble in alcohols, water and mixtures thereof and possess the known superb properties as auxiliaries in cosmetic hair preparations, for example as additives for hair lacquers or hairspray.

45 The polymer powders prepared in accordance with the invention can also be used as binders for transfer printing, as lubricant additives, as soil conditioners and as agrochemical seed-dressing

auxiliaries, in slow-release fertilizer formulations and in agricultural formulations with adhesion properties, as rust inhibitors or agents for removing rust from metallic surfaces, as scale inhibitors or scale removers, as auxiliaries in the 5 recovery of petroleum from oil-containing water and in the extraction and transportation of oil and natural gas, as agents releasing the active compound in pharmaceutical preparations, as cleaners for wastewaters, as raw materials for adhesives, as detergent additives and as auxiliaries in the photographic 10 industry, in immunochemicals and in cosmetic skin preparations.

The homopolymers and copolymers of vinylcaprolactam described in the context of the present invention no longer exhibit the phenomenon of precipitation at elevated temperature, but instead 15 form a stable latex above 35°C, which on cooling to below this temperature undergoes completely reversible transition to form a clear solution. As a consequence, these polymers are very easy to dry by means of conventional drying techniques.

20 Examples

The examples which follow serve to illustrate the invention. The K value in each example was determined on a 1% strength by weight solution in water at 25°C by the method of Fikentscher.

25

Example 1

A solution of 5 g of 2-acrylamido-2-methylpropanesulfonic acid in 50 g of water was adjusted to a pH of 7 using dilute sodium 30 hydroxide solution. 150 g of ethanol and 395 g of N-vinylcaprolactam were added to form a homogeneous solution (feed 1). Feed 2 was prepared from 2 g of tert-butyl perpivalate and 85 g of ethanol.

35 A homogeneous mixture of 100 g of N-vinylcaprolactam, 100 g of ethanol, 10 g of water and 0.5 g of tert-butyl perpivalate was introduced into a 2 l stirred vessel fitted with stirrer, heating device, reflux condenser, metering device, gas inlet and gas outlet, and the mixture was heated to 75°C while stirring and 40 passing in nitrogen. After the polymerization had commenced, which is evident from a rise in the viscosity of the initial charge, feeds 1 and 2 were run in simultaneously over the course of 3 hours. In order to remove residual monomer, post-polymerization was carried out by running in a solution of 45 4 g of tert-butyl perpivalate in 100 g of ethanol over a period of 8 h at 75°C and then maintaining the mixture at this temperature for a further 3 hours. In order to produce the purely

aqueous solution, 500 g of water were run in, and steam was passed in in order to distill off the ethanol at an internal temperature of 100°C at the end. A white polymer latex of low viscosity was obtained which on cooling became a clear, viscous 5 polymer solution.

The solution had a solids content of 35% by weight and a residual N-vinylcaprolactam content of < 50 ppm. The K value of the polymer was 34. Spray drying gave a white, odorless powder.

10

Examples 2 and 3

The procedure of Example 1 was followed using in each case 2% by weight of acrylic acid or methacrylic acid together with 98% by 15 weight of N-vinylcaprolactam as neutralized comonomers. Spray drying gave white powders having a K value in the range from 30 to 40.

Example 4

20

A solution of 4 g of 2-acrylamido-2-methylpropanesulfonic acid, 0.5 g of 4,4'-azobis(4-cyanopentanoic acid) and 2 g of thioglycolic acid in 100 g of water was adjusted to a pH of 7 using dilute sodium hydroxide solution (feed 1).

25

Polymerization was carried out using a 2 l stirred vessel fitted with stirrer, heating device, reflux condenser, metering device, gas inlet and gas outlet. The initial charge was a solution of 2 g of 2-acrylamido-2-methylpropanesulfonic acid, 0.5 g of 30 4,4'-azobis(4-cyanopentanoic acid) and 1 g of thioglycolic acid in 600 g of water, which charge was adjusted to a pH of 7 using dilute sodium hydroxide solution. Addition of 100 g of melted N-vinylcaprolactam followed by intense stirring gave an emulsion. This emulsion was heated to 90°C while passing in nitrogen. After 35 the polymerization had commenced, which is evident from the exothermic reaction, feed 1 and 200 g of melted N-vinylcaprolactam were run in simultaneously over the course of 3 hours.

40 In order to remove residual monomer, post-polymerization was carried out by running in a solution of the sodium salt of 0.5 g of 4,4'-azobis(4-cyanopentanoic acid) in 100 g of water over a period of 8 hours at 90°C and then maintaining the mixture at this temperature for a further 3 hours. In order to reduce the 45 residual monomer content further, a steam distillation was

10

carried out. A white polymer latex of low viscosity was obtained which on cooling became a clear, viscous polymer solution.

The solution had a solids content of 25% and a residual 5 N-vinylcaprolactam content of < 50 ppm. The K value of the polymer was 33. Spray drying gave a white, odorless powder.

Examples 5 and 6

10 The procedure of Example 1 was followed using in each case 2% by weight of acrylic acid or methacrylic acid together with 98% by weight of N-vinylcaprolactam as neutralized comonomers. Spray drying gave white powders having a K value in the range from 25 to 40. By varying the amount of regulator used it was possible to 15 obtain polymers with K values in the range from 15 to 200.

Example 7

A solution of 1 g of 4,4'-azobis(4-cyanopentanoic acid) in 50 g 20 of water was adjusted to a pH of 7 using dilute sodium hydroxide solution (feed 1).

Polymerization was carried out using a 2 l stirred vessel fitted with stirrer, heating device, reflux condenser, metering device, 25 gas inlet and gas outlet. The initial charge was a solution of 0.5 g of 4,4'-azobis(4-cyanopentanoic acid) and 3.5 g of sodium dodecyl sulfate in 600 g of water, which charge was adjusted to a pH of 7 using dilute sodium hydroxide solution. Addition of 100 g of melted N-vinylcaprolactam followed by intense stirring gave an 30 emulsion. This emulsion was heated to 90°C while passing in nitrogen. After the polymerization had commenced, which is evident from the exothermic reaction, feed 1 and a mixture of 200 g of melted N-vinylcaprolactam and 6.5 g of Tween®80 (sorbitan monooleate reacted with 20 mol of ethylene oxide, from 35 Atlas-Chemie) were run in simultaneously over the course of 3 hours.

In order to remove residual monomer, post-polymerization was carried out by running in a solution of the sodium salt of 0.5 g 40 of 4,4'-azobis(4-cyanopentanoic acid) in 100 g of water over a period of 8 hours at 90°C and then maintaining the mixture at this temperature for a further 3 hours. In order to reduce the residual monomer content further, a steam distillation was carried out. A white polymer latex of low viscosity was obtained 45 which on cooling became a clear, viscous polymer solution.

11

The solution had a solids content of 35% and a residual N-vinylcaprolactam content of 100 ppm. The K value of the polymer was 45. Spray drying gave a white, odorless powder.

5 Example 8

A solution of 5 g of 4,4'-azobis(4-cyanopentanoic acid) in 500 g of water was adjusted to a pH of 7 using dilute sodium hydroxide solution (feed 1).

10

Polymerization was carried out using a 3 l stirred vessel fitted with stirrer, heating device, reflux condenser, metering device, gas inlet and gas outlet. The polymerization was carried out batchwise, for which purpose a mixture of 1500 g of water, 70 g of feed 1, 400 g of N-vinylpyrrolidone and 400 g of melted N-vinylcaprolactam was prepared. A suspension was obtained by intense stirring, which was heated to an internal temperature of 90°C while passing in nitrogen. After the polymerization had commenced, which is evident from the exothermic reaction and the viscosity rise of the polymerization medium, feed 1 was run in over the course of 5 hours. During the polymerization the batch was diluted with about 1500 g of water. Subsequently, in order to reduce the residual monomer content, the batch was held at 90°C for a further 3 hours. In order to reduce the residual monomer content further, a steam distillation was carried out. A white polymer latex was obtained which on cooling became a clear polymer solution of high viscosity.

The solution had a solids content of about 19% by weight and a residual N-vinylcaprolactam content of 400 ppm. The K value of the polymer was 83. Spray drying from a highly dilute solution or roller drying gave a white, odorless powder.

Example 9

35

Following the procedure of Example 8, a 1:1 by weight mixture of N-vinylpyrrolidone and N-vinylcaprolactam in homogeneous solution in methanol was polymerized using t-butyl perpivalate as polymerization initiator. After replacing the solvent by water a white latex was obtained which on cooling became a viscous, clear solution.

The solution had a solids content of about 37% by weight and a residual N-vinylcaprolactam content of 500 ppm. The K value of the polymer was in the range from 60 to 70. Spray drying from a

0050/44512

2178328

12

highly dilute solution or roller drying gave a white, odorless powder.

5

10

15

20

25

30

35

40

45

We claim:

1. A process for preparing a pulverulent polymer based on
5 N-vinylcaprolactam by polymerizing
 - A) from 50 to 100% by weight of N-vinylcaprolactam with
 - B) from 0 to 50% by weight of further N-vinyllactams, heteroaromatic vinyl compounds, vinyl esters, C₁-C₁₀-alkyl acrylates or methacrylates, or a mixture thereof, and
 - C) from 0 to 5% by weight of monoethylenically unsaturated monomers containing acid groups,
- 15 which comprises subjecting the monomers A, B and C
 - (i) to polymerization in homogeneous, water-containing solution, which contains from 10 to 95% by weight of a water-miscible organic solvent, based on the water, or in a homogeneous mixture comprising from 0 to 90% by weight of water and from 100 to 10% by weight of methanol, in the presence of a free-radical initiator, and then replacing the organic solvent by water, or
 - (ii) to polymerization in aqueous emulsion in the presence of a free-radical initiator and in the presence or absence of an emulsifier
- 20 30 and subjecting the resulting aqueous polymer solutions or dispersions to a drying technique which is customary for such formulations, in order to produce a pulverulent polymer.
- 35 2. A process as claimed in claim 1, wherein polymerization in embodiment (ii) is carried out in the absence of a monomer C but in the presence of an emulsifier.
- 40 3. A process as claimed in claim 2, wherein polymerization in embodiment (ii) is carried out in the absence of a monomer C and in the presence of at least 30% by weight, based on the overall quantity of the monomers, of a further N-vinyllactam as monomer B in the absence of an emulsifier.

4. A process as claimed in any of claims 1 to 3 using the monomers C in the form of their alkali metal, alkaline earth metal or ammonium salts.
- 5 5. A process as claimed in any of claims 1 to 4, wherein the polymerization in accordance with embodiment (ii) is carried out with the additional use of a regulator to control the molecular weight.
- 10 6. A process as claimed in any of claims 1 to 5 using N-vinylpyrrolidone, N-vinylpiperidones, N-vinylimidazole, vinylpyridines or vinylpyridine N-oxides, vinyl acetate, vinyl propionate, methyl, ethyl or butyl acrylate or a corresponding methacrylate as monomers B.
- 15 7. A process as claimed in any of claims 1 to 6 using acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, 2-acrylamido-2-methylpropanesulfonic acid, vinylsulfonic acid, 3-sulfopropyl acrylate or methacrylate, or vinylphosphonic acid as monomers C.
- 20 8. A process as claimed in any of claims 1 to 7, which comprises polymerizing
 - 25 A) from 90 to 100% by weight of N-vinylcaprolactam with
 - B) from 0 to 10% by weight of the monomers B and
 - 30 C) from 0 to 5% by weight of the monomers C.
9. A process as claimed in any of claims 1, 4, 5 and 7, which comprises copolymerizing
 - 35 A) from 95 to 99.9% by weight of N-vinylcaprolactam with
 - C) from 0.1 to 5% by weight of the monomers C.
10. A process as claimed in any of claims 1, 2 and 5, which
 - 40 comprises homopolymerizing N-vinylcaprolactam A.
11. A process as claimed in any of claims 1 to 10, wherein the drying technique used to produce a pulverulent polymer is spray drying, fluidized-bed spray drying, roller drying, belt drying, freeze drying or freeze concentrating.

0050/44512

2178328

15

12. The use of a pulverulent polymer prepared as claimed in any of claims 1 to 11 as an auxiliary in cosmetic hair preparations or cosmetic skin preparations.

5

10

15

20

25

30

35

40

45

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

BLACK BORDERS

IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

FADED TEXT OR DRAWING

BLURRED OR ILLEGIBLE TEXT OR DRAWING

SKEWED/SLANTED IMAGES

COLOR OR BLACK AND WHITE PHOTOGRAPHS

GRAY SCALE DOCUMENTS

LINES OR MARKS ON ORIGINAL DOCUMENT

REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.